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RATE CONSTANTS FOR ELEMENTARY STEPS IN HYDROCARBON OXIDATION, (U)  
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## RATE CONSTANTS FOR ELEMENTARY STEPS IN HYDROCARBON OXIDATION

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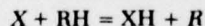
A review is given of the four main types of reaction which are important in determining the distribution of products in the oxidation of hydrocarbons:

- free-radical attack on the hydrocarbon RH;
- decomposition of the radical *R* by C-C homolysis;
- reaction of *R* radical with O<sub>2</sub> to form the conjugate alkene;
- reaction of *R* radical with O<sub>2</sub> to give O-heterocycles and other oxygenated products.

Rate constants for these types of reaction, obtained from studies of the oxidation of C<sub>2</sub>-C<sub>4</sub> hydrocarbons and neopentane, are applied to predict the yields of products in the oxidation of pentane.

During the past few years, product profiles and rate constants<sup>1</sup> for the elementary reactions involved have been obtained for a number of lower hydrocarbons and related compounds undergoing oxidation in the temperature range 440-500°C, where the mechanism is rather simpler than at lower temperatures. At about 500°C, four main types of reaction are important in determining the product distribution.

- Free-radical attack on the hydrocarbon.



- Decomposition of the radical *R* by C-C homolysis, this reaction becoming more important as the concentration of O<sub>2</sub> decreases and the temperature increases.
- Reaction of *R* radicals with O<sub>2</sub> to form the conjugate alkene, the yields varying between 50% (n-butane) and 95% (ethane) at normal O<sub>2</sub> concentrations.
- Reaction of *R* radicals with O<sub>2</sub> to give O-heterocycles and other oxygenated products. Although present in yields of only 5-10% with C<sub>2</sub>-C<sub>4</sub> hydrocarbons, the total yields of these compounds can rise to 50% with C<sub>5</sub> and C<sub>6</sub> alkanes.

Two other general types of reaction may also become important in appropriate circumstances. First, with relatively long alkyl radi-

cals, isomerisation by H-atom transfer may occur, although such reactions are usually slower<sup>1</sup> than the alternative reactions (ii)-(iv) listed above. Secondly, at high reaction rates, for example in cool flames, where radical concentrations are high, chain propagation may occur through radical-radical reactions. Such reactions, however, will not normally be important under the experimental conditions described in this paper.

This paper falls into two main sections. In the first, the information available for these reactions from studies with hydrocarbons other than n-pentane is reviewed. The second section examines the extent to which use of these constants enables a satisfactory prediction to be made of the product distribution obtained in the oxidation of n-pentane at 480°C.

### Types of Reaction in Hydrocarbon Oxidation

#### 1. Free-radical Attack on Hydrocarbons and Related Compounds

In general, at 400-500°C, the hydrocarbon is removed mostly by attack of OH and HO<sub>2</sub> radicals. In the presence of H<sub>2</sub>, attack by H atoms will also be important. With the devel-

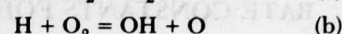
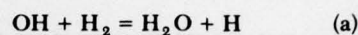
opment of E.S.R., resonance fluorescence, and other spectroscopic techniques, reliable rate constants are now available for  $H^2$  and  $OH^3$  reactions with hydrocarbons and related compounds, particularly at room temperature. At about  $500^\circ C$ , studies of the relative rate of loss of  $H_2$  and hydrocarbon, when traces of hydrocarbon are added to slowly reacting mixtures of  $H_2 + O_2$  in aged boric-acid-coated vessels (Method I), have given relative rate constants for  $H$  and  $OH$  attack.<sup>4</sup> The isolation of a 'clean' source of  $HO_2$  radicals has been a long-standing problem in hydrocarbon oxidation, since these radicals are usually accompanied by the more reactive  $OH$  radicals. The addition of hydrocarbons to slowly reacting mixtures of formaldehyde and  $O_2$  in KCl-coated vessels at  $440$ – $540^\circ C$  has recently been used to study reactions of  $HO_2$  radicals.<sup>5,6</sup> Below  $500^\circ C$ ,  $OH$  radicals are effectively absent because the hydrogen peroxide formed is efficiently destroyed at the vessel surface. Above  $500^\circ C$ , homogeneous decomposition of hydrogen peroxide occurs to a limited degree and a small correction for  $OH$  attack on the hydrocarbon is necessary.

Specific parameters (Table I) for radical attack can be obtained from an additivity rule based on the assumption that the contribution per C-H bond to the total rate constant is the same for all primary, all secondary, and all tertiary C-H bonds in each hydrocarbon. The overall rate constant  $k$  is then given by

$$k = n_p A_p \exp(-E_p/RT) + n_s A_s \exp(-E_s/RT) + n_t A_t \exp(-E_t/RT) \quad (i)$$

where  $n$  is the number of bonds of a specific type,  $A$  is the Arrhenius factor per C-H bond, and  $E$  is the corresponding activation energy. The subscripts  $p$ ,  $s$ ,  $t$  refer to attack at primary,

secondary, and tertiary C-H bonds, respectively. Table I also gives the specific rate constants for  $OH$  and  $H$  attack relative to reactions (a) and (b) respectively at  $480^\circ C$ . To obtain absolute values, rate constants for these reactions are required.



However, for the calculation of the proportions of each species of alkyl radical formed from the hydrocarbon, only the relative values of the rate constants for radical attack are required.

## 2. Decomposition of Alkyl Radicals by C-C Homolysis

Arrhenius parameters are available in the literature for the decomposition by C-C homolysis of *n*-propyl,<sup>8</sup> *n*-butyl,<sup>9</sup> *s*-butyl<sup>10</sup> and *i*-butyl<sup>11</sup> radicals; the values considered to be the most reliable are given in Table II. All the parameters are determined by the use of the rate constant for the appropriate radical-radical recombination. Although the rate constant for methyl radical recombination is now accurately known at room temperature<sup>1</sup> (the temperature coefficient is less well established experimentally), the values for other alkyl radicals are less certain, particularly in the case of the *t*-butyl radical where the reported values<sup>9</sup> range from  $10^5$  at low temperatures<sup>13</sup> to  $10^{8.5}$  at  $350^\circ C$ .<sup>14</sup> More recent studies<sup>15</sup> suggest that the low values may be in error and that the recombination rate constant for *t*-butyl is at least  $10^7$  even at low temperatures. The most reasonable estimate for the recombination rate

\*All values of rate constants are in litre mole second units, and  $R$  in  $\text{cal mole}^{-1} \text{K}^{-1}$ .

TABLE I  
Specific parameters (per C-H bond) for  $H$ ,  $OH$  and  $HO_2$  attack\*

|           | OH                 |                |                                    | H                    |                |                                  | HO <sub>2</sub> <sup>1</sup> |      |
|-----------|--------------------|----------------|------------------------------------|----------------------|----------------|----------------------------------|------------------------------|------|
|           | A <sup>3</sup>     | E <sup>3</sup> | $\frac{k(OH + RH)^7}{k(OH + H_2)}$ | A <sup>4</sup>       | E <sup>4</sup> | $\frac{k(H + RH)^7}{k(H + O_2)}$ | A                            | E    |
| primary   | $6.15 \times 10^8$ | 1.65           | 0.95                               | $2.2 \times 10^{10}$ | 9.7            | 6.5                              | $1.0 \times 10^9$            | 19.4 |
| secondary | $1.4 \times 10^9$  | 0.86           | 1.8                                | $5.0 \times 10^{10}$ | 8.35           | 45                               | $1.0 \times 10^9$            | 17.0 |
| tertiary  | $1.25 \times 10^9$ | -0.19          | 4.7                                | $8.7 \times 10^{10}$ | 7.0            | 165                              | $1.0 \times 10^9$            | 14.4 |

\*  $1 \text{ mol}^{-1} \text{s}^{-1}$  and  $\text{kcal mol}^{-1}$  units.



TABLE II  
 Alkyl radical decompositions<sup>a</sup>

| Reaction  | A/s <sup>-1</sup>      | E/kcal mol <sup>-1</sup>   | T/K     | k/s <sup>-1</sup> at 753 K | Ref. |
|---|------------------------|----------------------------|---------|----------------------------|------|
| n-C <sub>3</sub> H <sub>7</sub> → C <sub>2</sub> H <sub>4</sub> + CH <sub>3</sub>                     | 1.6 × 10 <sup>14</sup> | 30.1                       | 523-623 | 2.95 × 10 <sup>5</sup>     | 8    |
| n-C <sub>4</sub> H <sub>9</sub> → C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>5</sub>       | 2.5 × 10 <sup>13</sup> | 28.7                       | 430-520 | 1.19 × 10 <sup>5</sup>     | 9    |
| s-C <sub>4</sub> H <sub>9</sub> → C <sub>3</sub> H <sub>6</sub> + CH <sub>3</sub>                     | 7.3 × 10 <sup>14</sup> | 34.4                       | 533-613 | 7.55 × 10 <sup>4</sup>     | 10   |
| i-C <sub>4</sub> H <sub>9</sub> → C <sub>3</sub> H <sub>6</sub> + CH <sub>3</sub> <sup>b</sup>        | 2.8 × 10 <sup>12</sup> | 32.7                       | 543-598 | 9.1 × 10 <sup>2</sup>      | 11   |
| (CH <sub>3</sub> ) <sub>3</sub> C·CH <sub>2</sub> → i-C <sub>4</sub> H <sub>8</sub> + CH <sub>3</sub> |                        | k = 3.53 × 10 <sup>3</sup> | 762     |                            | 12   |

<sup>a</sup>Values re-calculated from original data<sup>1</sup>

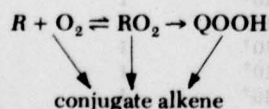
<sup>b</sup>Arrhenius A factor is probably too low

constant at about 500°C for an unspecified alkyl radical may be 10<sup>9±1</sup>; the values may decrease in the order primary > secondary > tertiary. Following suggestions in a recent review,<sup>1</sup> the recombination rate constant for primary radicals has been taken as 10<sup>10</sup> and that for secondary radicals as 10<sup>10.5</sup> exp(-3560/RT); a value for tertiary radicals will not be required in this paper. Since the recombination rate constant appears as a square root in the rate expression, an uncertainty in this rate constant of an order of magnitude is effectively reduced to a factor of 3 in the rate constant of the competing reaction.

### 3. Reaction of R Radicals with O<sub>2</sub> to Form Conjugate Alkene

At sub-atmospheric pressures in the temperature region of 300-500°C, with hydrocarbons where its formation is possible structurally, the conjugate alkene is the major primary product in the initial stages of reaction. Relatively few rate constants are available and the reaction path has only recently been elucidated. The conjugate alkene may be formed in at least three ways in the oxidation of R radicals:

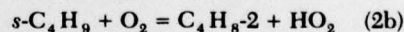
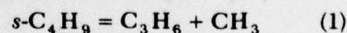
- By the direct bimolecular reaction  
 $R + O_2 = \text{alkene} + HO_2$  (2)
- Via decomposition of RO<sub>2</sub>.
- Via QOOH, formed by intramolecular H-atom transfer in the RO<sub>2</sub> radical.



If the conjugate alkene is formed by all three routes, the overall rate constant is extremely complex,<sup>16</sup> and under certain circumstances

may be dependent on mixture composition. Evidence against conjugate alkene formation from QOOH has been provided from a study<sup>17</sup> of the separate addition of small amounts of n-butane and cis-butene-2 to slowly reacting mixtures of H<sub>2</sub> + O<sub>2</sub>.

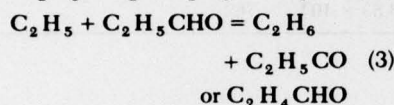
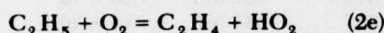
As R and RO<sub>2</sub> are effectively equilibrated under most conditions in the temperature range 400-500°C, routes (i) and (ii) for the formation of conjugate alkene cannot easily be distinguished and, for convenience, the direct bimolecular reaction R + O<sub>2</sub> will be assumed in this paper. Table III summarises the available rate data, which have been obtained in two ways. Method I involves measurement of the relative rates of formation of conjugate alkene and lower alkene when the hydrocarbon is added to slowly reacting mixtures of H<sub>2</sub> + O<sub>2</sub>. Thus with n-butane as additive, cis- and trans-butene-2 and propene are formed uniquely as primary products from the s-C<sub>4</sub>H<sub>9</sub> radical.



From measurements of the yields of propene and butene-2 over a range of mixture composition, the ratio  $k_1/k_{2b}$  is obtained. Using the known value of  $k_1$  (Table II),  $K_{2b} = 4.3 \times 10^7$  and  $7.8 \times 10^7$  at 480°C for the formation of cis- and trans-butene-2, respectively.<sup>23</sup> The analysis is more complex if the conjugate alkene can be formed from more than one species of alkyl radical, for instance propene from both n- and i-C<sub>3</sub>H<sub>7</sub> radicals and butene-1 from both n- and s-C<sub>4</sub>H<sub>9</sub> radicals. The proportion of conjugate alkene formed from each alkyl radical must then be calculated with the aid of the specific rate constants for H, OH, and HO<sub>2</sub> attack on the alkane<sup>23</sup> (Table I).

Values of  $k_2$  have also been determined from studies of the oxidation of aldehydes over the

temperature range 400–500°C (Method II). From measurements<sup>18</sup> of the relative yields of ethane and ethylene in the oxidation of propionaldehyde in aged boric-acid-coated vessels,  $k_2/k_3$  can be obtained. The absolute value of  $k_2$  can then be calculated by the use of the known<sup>26</sup> value of  $k_3$



Values of  $k_2$  for  $n\text{-C}_3\text{H}_7 + \text{O}_2$ <sup>20</sup> and  $i\text{-C}_3\text{H}_7 + \text{O}_2$ <sup>22</sup> have also been estimated in this way (Table III).

The rate constant ratios both from Method I and from Method II are accurate to within 10%, but the accuracy of the absolute values of  $k_2$  is limited by the uncertainty in the currently available rate constants for the radical cracking reactions (Table II), which depend on the radical-radical rate constants as discussed earlier. Accepting an order of magnitude uncertainty in the latter, then a possible error of 300% in the absolute values of  $k_2$  exists. The variation in  $k_2$  spans the range  $10^7 - 10^8$  and may be partly due to uncertainties in  $k_1$  and  $k_3$ . The agreement between the two values for  $n\text{-C}_3\text{H}_7 + \text{O}_2$  shows that Methods I and II give consistent results.

If reaction (2) proceeds by a direct bimolecular process, then an  $A$  factor of about  $10^9$  is likely, so that  $E_2$  will be small. Experimental confirmation comes from a combination of  $k_2$  for  $i\text{-C}_4\text{H}_9 + \text{O}_2$  at 480°C with the value at

40°C, obtained from a photo-oxidation study,<sup>25</sup> which gives  $E = 7.5 \text{ kcal mol}^{-1}$ ,  $A = 3.5 \times 10^9$ .

The role of surface in the formation of products in hydrocarbon oxidation has been discussed frequently. Knox<sup>27</sup> has suggested that in the oxidation of isobutane at 300°C, isobutene is formed in a homogeneous reaction but that the other products are formed in surface reactions of  $\text{RO}_2$ . Barnard,<sup>28</sup> however, found no pentenes in a shock-tube study of the oxidation of  $n$ -pentane at 650–850°C, where surface reactions should be unimportant, and suggests that this supports Pollard's view<sup>29</sup> that conjugate alkene is formed at the vessel surface. This interpretation can probably be discounted because radical decomposition reactions should dominate at the temperatures used by Barnard,<sup>28</sup> particularly at the rather low  $\text{O}_2$  pressures used, so that conjugate alkene would at most be a minor product. Recently, studies<sup>30</sup> of the addition of  $n$ -butane to slowly reacting mixtures of  $\text{H}_2 + \text{O}_2$  at 480°C using fresh and aged boric-acid-coated and 'clean' Pyrex vessels with diameters varying between 20 and 55 mm i.d. have shown that the ratios [conjugate alkene]/[lower alkene] and [conjugate alkene]/[O-heterocycle] are independent of vessel diameter and surface. It is thus unlikely that surface processes are involved in product formation at 480°C, and this conclusion almost certainly holds at higher temperatures. At lower temperatures, about 300°C, surface reactions of  $\text{RO}_2$ , and particularly  $\text{ROOH}$ , may play an important part in the formation of oxygenated products with a lower carbon number than the parent hydrocarbon.

TABLE III  
Rate constants for the formation of conjugate alkene

| Reaction                              | Product                               | $T/K$ | $k/1 \text{ mol}^{-1} \text{ s}^{-1}$ | Method                            | Ref.            |
|---------------------------------------|---------------------------------------|-------|---------------------------------------|-----------------------------------|-----------------|
| $\text{C}_2\text{H}_5 + \text{O}_2$   | $\text{C}_2\text{H}_4$                | 713   | $5.5 \times 10^7$                     | II                                | 18*             |
|                                       |                                       | 896   | $1.0 \times 10^8$                     | $\text{C}_2\text{H}_6/\text{O}_2$ | 19              |
| $n\text{-C}_3\text{H}_7 + \text{O}_2$ | $\text{C}_3\text{H}_6$                | 723   | $1.8 \times 10^7$                     | II                                | 20*             |
|                                       |                                       | 753   | $2.2 \times 10^7$                     | I                                 | 21*             |
| $i\text{-C}_3\text{H}_7 + \text{O}_2$ | $\text{C}_3\text{H}_6$                | 713   | $1.3 \times 10^8$                     | II                                | 22              |
| $n\text{-C}_4\text{H}_9 + \text{O}_2$ | $\text{C}_4\text{H}_8\text{-1}$       | 753   | $1.6 \times 10^8$                     | I                                 | 23              |
| $s\text{-C}_4\text{H}_9 + \text{O}_2$ | $\text{trans-C}_4\text{H}_8\text{-2}$ | 753   | $7.8 \times 10^7$                     | I                                 | 23              |
|                                       | $\text{cis-C}_4\text{H}_8\text{-2}$   | 753   | $4.3 \times 10^7$                     | I                                 | 23              |
| $i\text{-C}_4\text{H}_9 + \text{O}_2$ | $\text{C}_4\text{H}_8\text{-1}$       | 753   | $5.1 \times 10^7$                     | I                                 | 23              |
|                                       | $i\text{-C}_4\text{H}_8$              | 753   | $2.3 \times 10^7$                     | I                                 | 24 <sup>b</sup> |
|                                       |                                       | 313   | $1.7 \times 10^4$                     | Photo-oxidn.                      | 25*             |

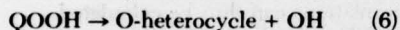
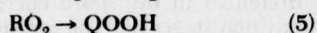
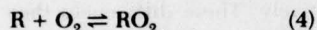
\*recalculated from the original data using the rate constants given in reference 1.

<sup>b</sup>preliminary value.

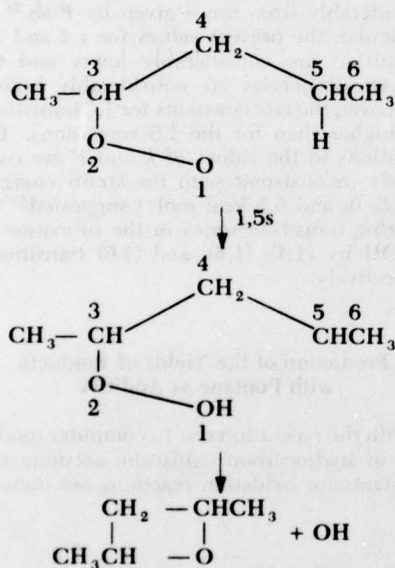


#### 4. Reaction of R Radicals with O<sub>2</sub> to Give O-Heterocycles

It is generally accepted that O-heterocyclic compounds are formed by the homogeneous formation and subsequent decomposition of the QOOH radical (PRID theory).<sup>1,16</sup>



Thus, for example, 1,5 H atom transfer in the 2-pentylperoxy radical will lead to 2,4-dimethyloxetan.



The letters p, s, t, are used to signify transfer of primary, secondary, and tertiary H atoms, respectively. Oxirans, oxetans, tetrahydrofurans (THF), and tetrahydropyrans are formed from (1,4), (1,5), (1,6), and (1,7) transfers, respectively. The relative rates of formation of the various QOOH radicals produced from a hydrocarbon are determined mainly by three factors:

- (i) the relative ease of attack at the various C—H bonds in the hydrocarbon;
- (ii) the strength of the C—H bond from which internal abstraction occurs;
- (iii) the strain energy in the formation of the ring transition state.

For the evaluation of  $k_5$ , very simple systems are required. The oxidation of neopentane is

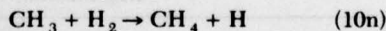
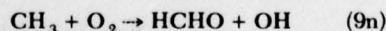
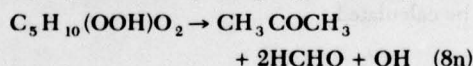
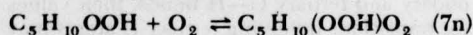
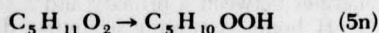
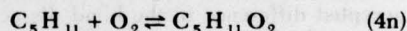
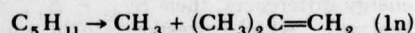
almost ideal in this respect. Only one species of alkyl radical is formed, and as conjugate alkene formation is not possible, the yield of oxygenated products is magnified. Further, at high temperatures, the neopentyl radical decomposes, and from measurements of the relative amounts of decomposition and oxygenated products, rate constants for the oxidation reactions may be calculated by the use of the known rate constant for the decomposition reaction. When traces of neopentane are added to slowly reacting mixtures of H<sub>2</sub> + O<sub>2</sub> at 753 K, the primary products, methane, formaldehyde, acetone, isobutene, and 3,3-dimethyloxetan (DMO) account for over 95% of the neopentane lost in the early stages of reaction.<sup>31</sup> Over a ten-fold range of O<sub>2</sub> pressure,

$$R_1 = \frac{([DMO] + [\text{acetone}])}{[\text{isobutene}]} \alpha [O_2] \quad (\text{ii})$$

and

$$R_2 = [\text{acetone}] / [DMO] \alpha [O_2] \quad (\text{iii})$$

The relationships are consistent with the mechanism:



Using stationary-state treatment, it can be shown<sup>31</sup> that reaction (5n) is effectively irreversible, otherwise the kinetic expression for  $R_1$  tends towards a square dependence on [O<sub>2</sub>] at high [O<sub>2</sub>] in direct contrast to the experimental observation that dependence on [O<sub>2</sub>] falls slightly at high oxygen concentrations. As reaction (4n) is effectively equilibrated, then  $R_1$  in equation (ii) is given by

$$R_1 = K_{4n} k_{5n} [O_2] / k_{1n} \quad (\text{iv})$$

Using the value of  $k_{1n}$  given in Table II and  $K_{4n} = 86$  at 753 K from thermochemical data, then  $k_{5n} = 1.8 \times 10^4$ . Benson<sup>32</sup> suggests that  $A_{5n} = 10^{12.1}$  so that  $E_{5n} = 27 \text{ kcal mol}^{-1}$ .

By the use of *n*-butane and *cis*- and *trans*-butene-2 as separate additives to the  $H_2 + O_2$  reaction (Method I), values of  $k_5$  for (1,4p), (1,4s) (epoxybutane) and (1,6p)(THF) transitions have been obtained at 753 K.<sup>17</sup> In all cases, equations similar to equation (iv) in the neopentane studies are obtained from the results and a knowledge of the values of  $k_1$  and  $K_4$  for *s*-butyl and *n*-butyl radicals is required (Table II). The values of  $k_5$  are summarised in Table IV.

Several features in Table IV merit further comment.

(i) The value for  $k_5$  (1,5p) from neopentane is consistent with  $k_5$  (1,4p) and  $k_5$  (1,6p) from *n*-butane and this suggests that the rate constants in Table IV may be used to a first approximation, at least, for the general reaction  $RO_2 \rightarrow QOOH$ .

(ii) The ratio  $k_5$  (1,4s)/ $k_5$  (1,4p)  $\approx$  11. As both rate constants were obtained from reactions of the *s*-butyl radical, no error is introduced into the ratio by uncertainty in radical recombination rate constants. Similar *A* factors are expected for the transitions because the entropy changes are small and almost identical, so if the ratio of 11 arises solely from activation energy differences, then  $E_{1,4p} - E_{1,4s} = 3.5$  kcal mol<sup>-1</sup>, which corresponds to the normally accepted difference in the bond dissociation energies between a primary and a secondary C—H bond. Assuming a similar difference between the bond dissociation energies of secondary and tertiary C—H bonds, then values for transitions involving tertiary H atoms may be calculated.

(iii) For transitions involving a primary H atom, the change from a 1,4 to a 1,5 transition increases the rate constant by a factor of 8.2 and by a further factor of 3.3 for the change from 1,5 to a 1,6 transition. For equal *A* factors these increases correspond to activation energy differences of 3.1 and 1.8 kcal mol<sup>-1</sup>, respectively. These differences then correspond to differences in the strain energy in the ring transition stages and the remaining 1,4 to 1,6 transitions can thus be calculated.

(iv) The absolute activation energies are based on an *A* factor of  $10^{12.1}$ , which has been suggested by Benson<sup>32</sup> for the 1,5p transition involved in reaction (5n).

(v) The rate constants for reaction (5) differ considerably from those given by Fish.<sup>33</sup> In particular, the present values for 1,4 and 1,5 transitions are considerably lower and the activation energies are considerably higher. Moreover, the rate constants for 1,6 transitions are higher than for the 1,5 transitions. The variations in the values of *k* and *E* are completely inconsistent with the strain energies of 6.5, 0, and 6.5 kcal mol<sup>-1</sup> suggested<sup>33</sup> for the ring transition states in the formation of QOOH by (1,4), (1,5), and (1,6) transitions, respectively.

#### Prediction of the Yields of Products with Pentane as Additive

With the recent interest in computer modelling of hydrocarbon oxidation, accurate rate constants for oxidation reactions are increas-

TABLE IV  
Rate constants for the formation of QOOH radicals

| C—H bond broken | Type of H-atom transfer | Estimates <sup>a</sup> by Fish <sup>33</sup> |                                    | Experimental values <sup>b</sup>   |                                    |
|-----------------|-------------------------|--|------------------------------------|------------------------------------|------------------------------------|
|                 |                         | <i>E</i><br>kcal mol <sup>-1</sup>           | <i>k</i> /s <sup>-1</sup> at 753 K | <i>E</i><br>kcal mol <sup>-1</sup> | <i>k</i> /s <sup>-1</sup> at 753 K |
| primary         | 1,4p                    | 21   | $1.5 \times 10^5$                  | 30                                 | $2.2 \times 10^3$                  |
|                 | 1,5p                    | 15   | $6.5 \times 10^6$                  | 27                                 | $1.8 \times 10^4$                  |
|                 | 1,6p                    | 21   | $1.0 \times 10^5$                  | 25                                 | $6.0 \times 10^4$                  |
| secondary       | 1,4s                    | 17   | $1.5 \times 10^6$                  | 26.5                               | $2.4 \times 10^4$                  |
|                 | 1,5s                    | 11   | $6.0 \times 10^7$                  | 23.5                               | $2.0 \times 10^5$                  |
|                 | 1,6s                    | 17   | $1.5 \times 10^6$                  | 21.5                               | $6.5 \times 10^5$                  |
| tertiary        | 1,4t                    | 14   | $8.0 \times 10^6$                  | 23                                 | $2.6 \times 10^5$                  |
|                 | 1,5t                    | 8  | $4.0 \times 10^6$                  | 20                                 | $2.2 \times 10^6$                  |
|                 | 1,6t                    | 14   | $8.0 \times 10^6$                  | 18                                 | $7.1 \times 10^6$                  |

<sup>a</sup>Fish assumes  $A = 10^{11}$  s<sup>-1</sup>.

<sup>b</sup>Activation energies obtained from rate constants using  $A = 10^{12.1}$  s<sup>-1</sup>.

ingly in demand. As the variety of systems is unlimited, the development of rate constants for use generally is of the utmost importance. Indeed, a comprehensive coverage of rate data for all conceivable reactions in hydrocarbon oxidation is still a distant target and may indeed be unnecessary for many purposes. For the pentane +  $O_2$  system, no specific rate constants except for H and OH +  $C_5H_{12}$  are available for the four main types of reaction listed at the beginning of the paper. It is, therefore, intended to investigate how closely the data given in Tables I-IV, obtained from studies of oxidation of  $C_2$ - $C_4$  hydrocarbons and neopentane, can predict the yields of the products when 1% of pentane is added to slowly reacting mixtures of  $H_2 + O_2$  at 753 K. In this preliminary analysis, only the yields of the main primary products at 10% loss of pentane will be considered.

Figure 1 shows the yields of the main early products and the initial gradients show that they are all primary products. The 10% yields are summarised in Table V. Conjugate alkenes, cracking products and O-heterocycles are the major products. The pentenes are formed in the direct bimolecular reaction between R and  $O_2$ , methane, ethylene, propene, and butene-1 by radical cracking reactions, and the ring compounds 1,2-epoxybutane (1,2EB), 2,3-epoxybutane (2,3EB), 2-ethyloxetan (2EO), 2,4-dimethyloxetan (2,4DMO), 2-methyltetrahydrofuran (2-MTHF) and tetrahydropyran (THP) by formation and subsequent decomposition of QOOH radicals. Figure 2 shows the reaction pathways for the formation of these products from the three pentyl radicals. At this stage, it is assumed that the QOOH radicals decompose uniquely to give an O-ring compound and the OH radical.

For comparison with the experimental results, the predicted yields of products from the three pentyl radicals are calculated as follows.

(i) A computer program is used which incorporates a comprehensive mechanism for the  $H_2 + O_2$  reaction and the major reactions occurring when traces of pentane are added. The specific parameters (Table I) for attack by H, OH, and  $HO_2$  on the hydrocarbon are used in equation (i), and allowance is also made for minor attack by O atoms. For the mixture used, the percentages of 1-, 2-, and 3-pentyl radical formed after 10% loss of neopentane are estimated as 22, 52, and 26%, respectively.

(ii) The rate constant for the homolysis of both the 1- and the 2-pentyl radical is assigned the value given in Table II for the n-butyl radical,

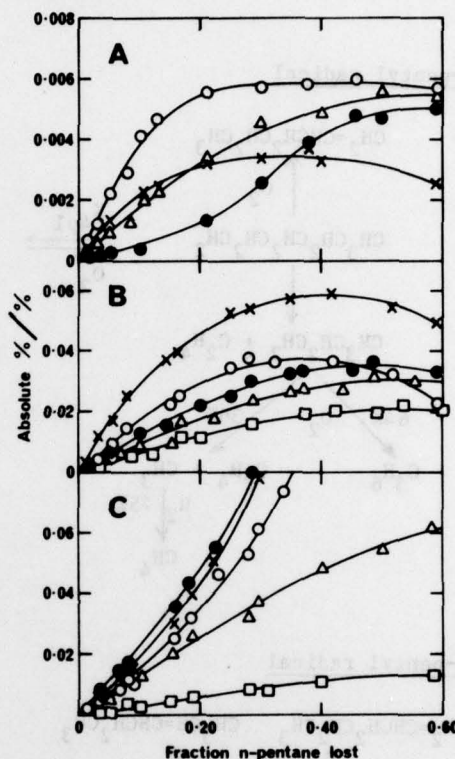


FIG. 1. Variation of products with loss of n-pentane.  $H_2 = 140$ ,  $O_2 = 70$ ,  $N_2 = 285$ , n-pentane = 5 mm Hg;  $T = 753$  K. Part A:  $\circ$ , 2,3-epoxypentane;  $\times$ , 2-ethyloxetan;  $\Delta$ , tetrahydropyran;  $\bullet$ , 1,2-epoxypentane. Part B:  $\circ$ , pentene-1;  $\times$ , cis- and trans-pentene-2;  $\Delta$ , 2,4-dimethyloxetan;  $\bullet$ , 2-methyltetrahydrofuran;  $\square$ , butene-1. Part C:  $\circ$ , methane;  $\times$ , ethylene;  $\bullet$ , propene;  $\Delta$ , acetaldehyde;  $\square$ , propionaldehyde.

and that for the 3-pentyl radical is the value given for s-butyl radicals.

(iii) The rate constants for pentene formation are taken as the values for the structurally analogous reactions of the s- and n-butyl radicals with  $O_2$  (Table III).

(iv) The value of the equilibrium constants (see Figure 2,)  $K_{4p1} = 459$ ,  $K_{4p2} = 637$ , and  $K_{4p3} = 210$  at 753 K, are calculated from thermochemical data.

(v) Rate constants for the isomerisation reaction  $RO_2 \rightarrow QOOH$  are given in Table IV. As no value for a 1,7p transition is available, a value of  $9.1 \times 10^4$  is assigned. This value predicts the correct yield of tetrahydropyran, with the particular rate constants used for the other reactions.



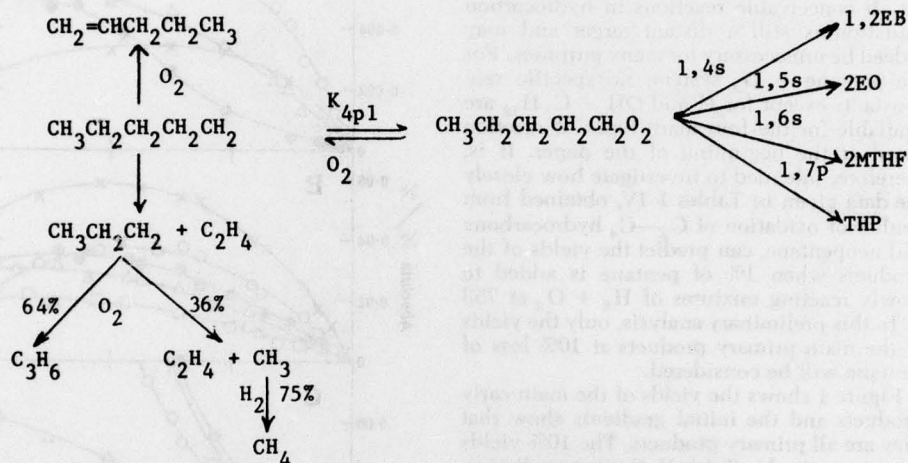
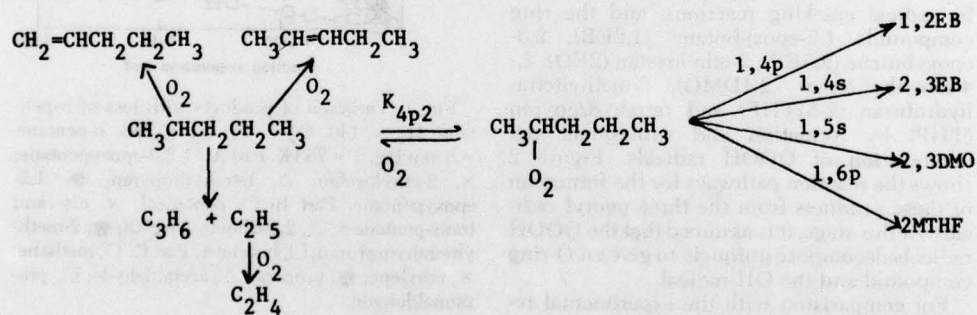
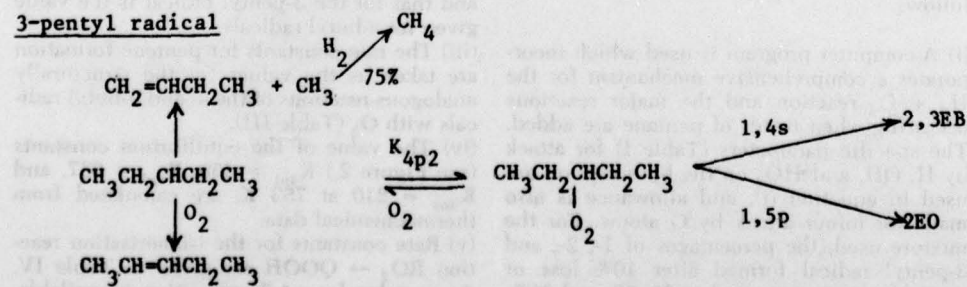
1-pentyl radical2-pentyl radical3-pentyl radical

FIG. 2. Reaction scheme for pentyl radicals.

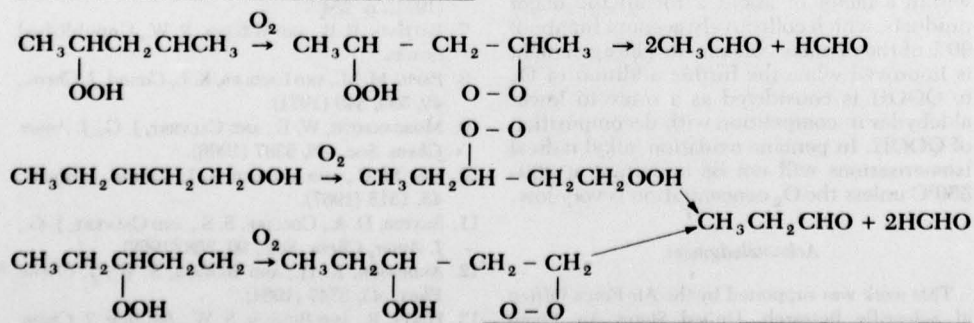
(vi) From previous studies, it is known that with the mixture used 64% of  $n\text{-C}_3\text{H}_7$  radicals react with  $\text{O}_2$  to give propene and 36% decompose to give ethylene and  $\text{CH}_3$  radicals,<sup>21</sup> of which 75% react with  $\text{H}_2$  to form methane.<sup>21</sup>

With the above data, the relative yields of product from each pentyl radical may be calculated, and the yields aggregated. The calculated percentage yields are shown in Table V, together with the experimental yields at 10% loss of pentane; the agreement is within a factor of about 2 for all products. Clearly, by minor adjustments of appropriate rate constants, the agreement could be improved considerably, particularly in the relative yields of the pentenes and in the total yields of cracking products which is slightly too high. The yields of O-heterocycles are closely predicted, with the possible exception of the two oxetans, whose experimental yields are lower than calculated by a factor of two. When the  $\text{O}_2$  concentration is increased, the difference between the predicted and experimental yields of the oxetans increases significantly. Moreover, the experimental yield of acetaldehyde (about 10% with the mixture presently being discussed) and of propionaldehyde (about 1.5%) increases with  $[\text{O}_2]$ . To a close approximation,

$$\frac{d[\text{CH}_3\text{CHO}]}{d[2,4\text{DMO}]} \propto [\text{O}_2]$$

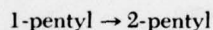
$$\text{and } \frac{d[\text{C}_2\text{H}_5\text{CHO}]}{d[2\text{EO}]} \propto [\text{O}_2]$$

which suggests that the addition of  $\text{O}_2$  to QOOH competes with decomposition of QOOH to give oxetans. A similar conclusion is reached in the neopentane addition studies where the  $[\text{acetone}]/[\text{3,3-dimethyloxetan}]$  ratio is directly proportional to  $[\text{O}_2]$ . It thus appears likely that the following reactions are important.



If the aldehydes are formed from the QOOH +  $\text{O}_2$  reaction, then the 1,5 H-transfers in pentane oxidation lead to both oxetans and aldehydes. Therefore, in Table V, the experimental yield of 2,4 dimethyloxetan should be increased by 50% of the acetaldehyde yield (if two molecules of acetaldehyde are formed from each QOOH +  $\text{O}_2$  reaction), and the experimental yield of propionaldehyde should be added to that of 2-ethyloxetan. The corrected figures, shown in brackets, considerably improve the agreement between calculated and experimental yields. There is no evidence that the other QOOH radicals react with  $\text{O}_2$  at a rate competitive with that of decomposition.

A final consideration is the role played by alkyl radical isomerisation. In the pentane system, the only important isomerisation will be



for which Arrhenius parameters of  $A = 1.0 \times 10^{11}$  and  $E = 20.3 \text{ kcal mol}^{-1}$  have been reported.<sup>34</sup> At 753 K, the rate constant is  $1.3 \times 10^3$ . With the isomerisation incorporated into the mechanism, the proportions of 1-, 2-, and 3-pentyl radicals produced at 10% loss of pentane are effectively modified slightly to 20.2, 53.8, and 26%, respectively. The modified relative yields of products are shown in Table V, and it is clear that isomerisation reactions will be unimportant in pentane oxidation under normal conditions unless the rate constants are considerably higher than suggested above.

It must be emphasised that this discussion relates to the distribution of initial products and not to the progress of reaction with time. As the products, alkenes and oxygenated compounds, are more reactive than the parent hydrocarbon, the development of the reaction with time will be governed also by the reactions of these products, and in particular at temperatures around 500°C by the build-up

TABLE V  
Predicted and experimental yields of products from pentane  
 $O_2 = 70$ ,  $H_2 = 140$  n-pentane = 5,  $N_2 = 285$  mm Hg;  $T = 753$  K

|                    | Predicted yields               |                                |                                |                   | Exptl.<br>yield<br>at 10%<br>loss | Predicted<br>yield with<br>isomerisation |
|--------------------|--------------------------------|--------------------------------|--------------------------------|-------------------|-----------------------------------|--|
|                    | 1-pentyl<br>(22%) <sup>a</sup> | 2-pentyl<br>(52%) <sup>a</sup> | 3-pentyl<br>(26%) <sup>a</sup> | Total<br>yield    |                                   |  |
| pentene-1          | 5.15                           | 6.1                            | —                              | 11.25             | 17.3                              | 11.0                                     |
| pentene-2          | —                              | 14.5                           | 17.4                           | 31.9              | 25.7                              | 32.4                                     |
| butene-1           | —                              | —                              | 7.3                            | 7.3               | 5.8                               | 7.3                                      |
| propene            | 1.7                            | 9.6                            | —                              | 11.3              | 19.2                              | 11.5                                     |
| ethylene           | 3.5                            | 9.6                            | —                              | 13.1              | 15.8                              | 13.2                                     |
| methane            | 0.7                            | —                              | 5.5                            | 6.2               | 11.5                              | 6.1                                      |
| 1,2-epoxybutane    | 0.35                           | 0.17                           | —                              | 0.52              | 0.41                              | 0.50                                     |
| 2,3-epoxybutane    | —                              | 1.85                           | 0.73                           | 2.58              | 2.98                              | 2.64                                     |
| 3-ethyloxetan      | 2.97                           | —                              | 0.54                           | 3.51              | 1.88<br>(3.45) <sup>b</sup>       | 3.27                                     |
| 2,4-dimethyloxetan | —                              | 15.2                           | —                              | 15.2              | 7.3<br>(12.8) <sup>c</sup>        | 15.8                                     |
| 2-methylTHF        | 9.61                           | 4.6                            | —                              | 14.2              | 10.4                              | 13.6                                     |
| THP                | 1.35                           | —                              | —                              | 1.35 <sup>d</sup> | 1.35                              | 1.25                                     |

<sup>a</sup>percentage of pentyl radical formed from n-pentane

<sup>b</sup>includes yield of  $C_2H_5CHO$  (see text)

<sup>c</sup>includes 50% of yield of  $CH_3CHO$  (see text)

<sup>d</sup>k (1,7p) chosen to predict yield exactly

of  $H_2O_2$  which is likely to play an important role as a secondary initiation (degenerate branching) agent.

#### Summary

Rate constants, obtained mainly from studies of  $C_2-C_4$  hydrocarbons and neopentane, for reactions of major importance in hydrocarbon oxidation at 400–550°C have been summarised. The rate constants (without modification) have been used to predict the yields of products formed when pentane is added to slowly reacting mixtures of  $H_2 + O_2$ . The agreement between predicted and experimental yields is within a factor of about 2 for all the major products, which collectively account for about 90% of the pentane consumed. The agreement is improved when the further addition of  $O_2$  to QOOH is considered as a route to lower aldehydes in competition with decomposition of QOOH. In pentane oxidation, alkyl radical isomerisations will not be important at 400–550°C unless the  $O_2$  concentration is very low.

#### Acknowledgment

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## COMMENTS

D. M. Golden, SRI, USA. Do you ever observe or consider pressure effects on radical cracking reactions? It is worthy of note that the A factors for the HO<sub>2</sub> abstraction reactions which you have presented are higher than those for OH abstraction from the same molecules. This is despite the fact that the activation energies are higher as well and the expectation that since OH is a diatomic species, it should exhibit the higher A factor.

**Authors' Reply.** We observe no pressure effects on alkyl radical cracking reactions in our studies of H<sub>2</sub> + O<sub>2</sub> + N<sub>2</sub> + hydrocarbon mixtures over the range 250-760 mmHg. In the aldehyde oxidation

work, pressure effects are observed up to about 200 mmHg. Our values of A (per C-H bond) for HO<sub>2</sub> + alkane are assumed, since  $k(\text{HO}_2 + \text{alkane})$  was only determined at 480°C. Combination of our results at 480°C with those of Alcock and Mile<sup>1</sup> at 100°C give an A factor (per C-H bond) of  $5 \times 10^7$  to  $1.0 \times 10^8 \text{ l} \cdot \text{mol}^{-1} \text{ s}^{-1}$  and  $E = 10.0 \text{ kcal mol}^{-1}$  for HO<sub>2</sub> attack at a tertiary C-H bond.

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| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br><b>MECHANISM OF HYDROCARBON OXIDATION    REACTION OF ALKYL + OXYGEN<br/>RATE CONSTANTS FOR ALKENE OXIDATION    CONJUGATE ALKENE<br/>REACTIONS OF H ATOM WITH RH    RATE CONSTANTS FOR ALKYL<br/>REACTIONS OF OH RADICALS WITH RH    RADICAL DECOMPOSITION<br/>REACTIONS OF HO<sub>2</sub> RADICALS WITH RH    ISOMERISATION OF ALKYL RADICALS</b>   |                       |   |  |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (cont)<br><b>A review is given of the four main types of reaction which are important in determining the distribution of products in the oxidation of hydrocarbons: (a) free-radical attack on the hydrocarbon RH; (b) decomposition of the radical R by C-C homolysis; (c) reaction of R radical with O<sub>2</sub> to form the conjugate alkene; (d) reaction of R radical with O<sub>2</sub> to give O-heterocycles and other oxygenated products. Rate constants for these types of reaction, obtained from studies of the oxidation of C<sub>2</sub>-C<sub>4</sub> hydrocarbons and neopentane, are applied to predict the yields of products in the oxidation of pentane.</b> |                       |   |  |

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REACTIONS ALKYLPEROXY RADICALS  
REACTIONS OF ALKYLHYDROPEROXIDE RADICALS

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